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AN IMPROVED SYNTHESIS OF p-BIS(PHENYL-
GLOYOXALOYL)-BENZENE

Stanley E. Wentworth

Army Materials and Mechanics Research Center
Watertown, Massachusetts

February 1973

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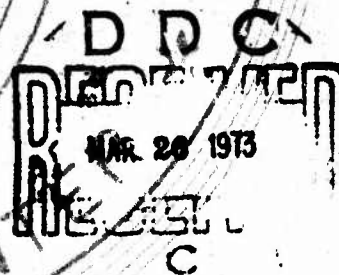
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Technical Report by
STANLEY E. WENTWORTH

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13. ABSTRACT An improved synthesis of p-bis(phenylglyoxaloyl)benzene (BPG), one of the co-monomers for the high temperature resistant polyphenylquinoxaline system, has been achieved. The method consists of three simple, high yield steps leading to a 70% overall yield of BPG. The starting material, phenylacetylene, is quantitatively converted to its cuprous salt which is then coupled with p-diiodobenzene to give p-bis(phenylethynyl)benzene in 73% yield. The diacetylene is oxidized to BPG in 96% yield using N-bromosuccinimide in dimethylsulfoxide. (Author)			

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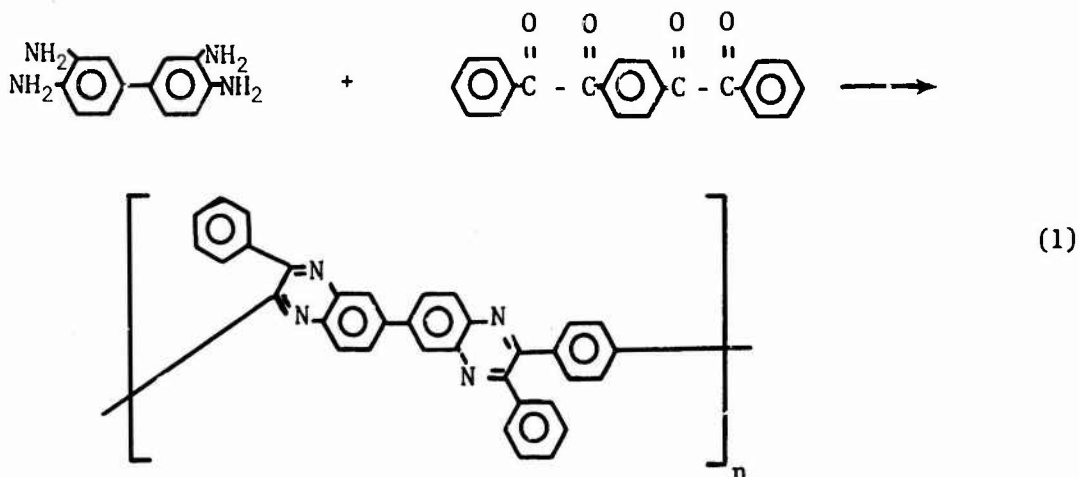
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I. INTRODUCTION

Polyphenylquinoxaline (PPQ) is one of the best of the currently available high temperature resistant resin systems. Potential areas of use are as fiber, resin matrix for advanced composites and as a structural adhesive, all areas of interest to the Army.

One of the most useful PPQ's is prepared by the condensation of 3,3'-diaminobenzidine and p-bis(phenylglyoxaloyl)benzene as shown in Eq. (1).¹



This material possesses superior thermal properties and is easily processed into usable forms. Its chief drawback is its expense which results from the high cost of the p-bis(phenylglyoxaloyl)benzene used in its preparation. This is due to the rather complex synthetic route currently used to produce the material.² We, therefore, sought to eliminate this drawback by devising a more efficient, less costly synthesis of this compound. Such a synthesis is the subject of this report.

II. DISCUSSION

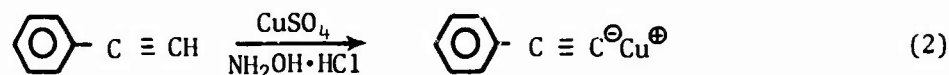
The p-bis(phenylglyoxaloyl)benzene has been prepared in three simple steps from readily available starting materials in 70% overall yield.

The first step is the preparation of cuprous phenylacetylide in quantitative yield from phenylacetylene according to the procedure of Castro et al.³

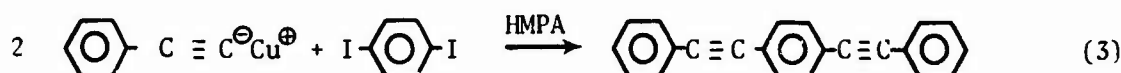
¹WRASIDLO, W. J., and AUGL, J. M. *Phenylated Polyquinoxalines from 1,4-bis(phenylglyoxaloyl)benzene*. Journal of Polymer Science, part B, v. 7, 1969, p. 281-286.

²AUGL, J. M., and WRASIDLO, W. J. *Synthesis and Evaluation of New Phenylated Polyquinoxalines*. Naval Ordnance Laboratory, NOLTR 69-120, 2 October 1969.

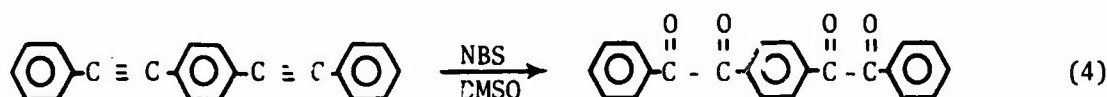
³CASTRO, C. E., GAUGHAN, E. J., and OWSLEY, D. C. *Indoles, Benzofurans, Phthalides and Tolans via Copper (I) Acetylides*. Journal of Organic Chemistry, v. 31, 1966, p. 4071-4078.



The second step is the coupling of two molecules of the copper salt with p-diiodobenzene to give p-bis(phenylethynyl)benzene in 73% yield using a modification of the procedure described by Castro et al.,³ see Eq. (3). In their preparation Castro and co-workers used pyridine as the solvent and achieved a 45% yield. We have found replacement of the pyridine with hexamethylphosphoramide results in the 73% yield indicated.



The crucial final step in our synthesis of p-bis(phenylglyoxaloyl)benzene is the nearly quantitative conversion of the diethynyl compound to the tetraketone using N-bromosuccinimide in dimethylsulfoxide, see Eq. (4). Though not specifically applied to p-bis(phenylglyoxaloyl)benzene, this method has been described by Wolfe et al.⁴ In addition to its high yield, this reaction



is exceedingly simple to run. The components are simply stirred together overnight, poured into water and the crude material isolated by filtration (see section III, Experimental).

III. EXPERIMENTAL

A. Cuprous Phenylacetylide

This compound was prepared from redistilled phenylacetylene using the procedure of Castro et al.³

B. P-bis(phenylethynyl)benzene

In a 250-ml three-neck flask fitted with a mechanical stirrer, a gas inlet and an air condenser connected to a mercury valve (to maintain a positive argon pressure) was placed 5.0 g of cuprous phenylacetylide, 5.05 g p-diiodobenzene and 125-ml hexamethylphosphoramide (stored over 4A molecular sieves). After flushing with argon, the mixture was heated with stirring to a bath temperature of 125 C under a continuous argon sweep for 16 hours. The mixture was then poured into

⁴WOLFE, S., PILGRIM, W. R., GARRARD, T. F., and CHAMBERLAIN, T. F. *N-Bromosuccinimide-Induced Dimethylsulfoxide Oxidation of Acetylenes*. Canadian Journal of Chemistry, v. 49, 1971, p. 1099-1105.

800-ml of water and the crude product isolated by filtration. Recrystallation from n-heptane yielded 3.10 g (73%) of p-bis(phenylethynyl)benzene melting at 172 to 176 C (178-179 C per Reference 3).

C. P-bis(phenylglyoxaloyl)benzene

In a 50-ml single-neck flask fitted with a magnetic stirrer and a drying tube was placed 30-ml of dimethylsulfoxide (freshly distilled from CaH_2), 1.0 g of p-bis(phenylethynyl)benzene and 2.58 g of N-bromosuccinimide (stored in a desiccator over P_2O_5). After stirring overnight, the solution was poured into 200-ml of water. The resulting precipitate was removed by filtration and air dried to yield 1.18 g (96%) of material whose IR spectrum (Perkin-Elmer Model 137) was identical with that of an authentic sample of p-bis(phenylglyoxaloyl)-benzene with the exception of two small additional bands attributable to dimethylsulfoxide. Recrystallation from ethanol with charcoal treatment gave highly purified material melting at 127 to 128.5 C (Reference 2 shows 123-124 C).

IV. CONCLUSIONS

As stated in the Introduction, the chief purpose in undertaking this investigation was to develop a less costly preparative route to p-bis(phenylglyoxaloyl)-benzene. Although the route described above uses rather costly starting materials, we feel that there is a good likelihood it will meet the stated objective. The materials cost should be more than offset by the reduced production costs which accrue from the high yield and simplicity embodied in this procedure.

Future work in this program will be devoted to the extension of this process to the preparation of tetraketones containing other functional groups such that crosslinking of the resin can be achieved.

The material contained in this report is the subject of a patent application which has been filed with the U. S. Patent Office on 5 September 1972.

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